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HEAT OF ADSORPTION OF IONS ON

X64 10159\*

METALS: LOW COVERAGE

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Classical image charge theory is inadequate to explain even the adsorption heats obtained for alkali metals on tungsten. This communication proposes an equation for calculating the heat of adsorption of any ion on any metal at coverages sufficiently low to allow the neglect of interactions between neighboring adsorbed ions. The adsorption energies arise from the superposition of (1) the interaction  $\phi_1$  of the net ionic charge with the metal and (2) a Van der Waals type interaction  $\phi_w$  of the instantaneous dipole moment of the ion with the metal.

For  $\phi_1$  it is necessary to use a quantum mechanically corrected image charge expression, since the ions approach to within 1/2 to 2 angstroms of the metal surface. Sachs and Dexter<sup>1</sup> have proposed such an expression:

$$\phi_1 = \frac{e^2}{4R} - \beta \kappa^{1/2} \frac{e^2}{4R^2}, \quad (1)$$

where  $R$  is the distance from the surface to the center of the ion,

$$\kappa = -\frac{1}{3} \left( \frac{3}{8\pi} \right)^{1/3} n_o^{-2/3} + \frac{(2\pi)^2}{6} \left( \frac{3}{8\pi} \right)^{2/3} a_o n_o^{-1/3}, \quad (2)$$

$n_o$  is the free electron density of the metal,  $a_o$  is the Bohr radius, and  $\beta$  is a constant. The energy arising from the polarization of an

<sup>1</sup>R. G. Sachs and D. L. Dexter: Jour. Appl. Phys. 21, 1304 (1950).

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adsorbed particle has been studied by Prosen and Sachs<sup>2</sup> and is given by

$$\phi_w = \frac{\alpha e^2 \pi k_m}{(2\pi)^3} \frac{\ln(2k_m R)}{R^2}, \quad (3)$$

where  $\alpha$  is the electronic dipole polarizability of the adsorbate and

$$k_m = (3\pi^2 n_0)^{1/3}. \quad (4)$$

Adding (1) and (3), gives the complete expression for the heat of adsorption of ions on a metal at zero coverage:

$$\phi = \frac{e^2}{4R} - \beta \kappa^{1/2} \frac{e^2}{4R^2} + \frac{\alpha e^2 \pi k_m^2}{(2\pi)^3} \frac{\ln(2k_m R)}{R^2}. \quad (5)$$

Implicit in Eq. (5) and in the choice of ionic values of polarizability (Table I) has been the assumption that a particle which desorbs as an ion must have had the properties of an ion prior to desorption. Hughes<sup>3</sup> in his adsorption lifetime studies has found evidence to support this.

The free electron density for tungsten is one per  $105 a_0^3$ , based on a lattice constant of  $3.16 \text{ \AA}$  and the assumption of one free electron per atom. For rhenium,  $n_0$  is one per  $100 a_0^3$  against with the assumption of one free electron per atom and lattice constants  $a = 2.76 \text{ \AA}$  and  $c = 4.46 \text{ \AA}$ . In the absence of a reported value for the polarizability of singly ionized barium, an approximation was necessary. The polarizability is a function of both the electron distribution and particle size. Since barium has the same electron distribution as cesium except for an

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<sup>2</sup>E. J. R. Prosen, and R. G. Sachs, Phys. Rev. 61, 65 (1942).

<sup>3</sup>F. L. Hughes, Phys. Rev. 113, 1032 (1959).

extra electron, the approximation used was

$$\frac{\alpha(\text{Ba}^+)}{\alpha(\text{Cs}^0)} = \frac{\alpha(\text{Ba}^{++})}{\alpha(\text{Cs}^+)} \quad (6)$$

where  $\alpha(\text{Ba}^{++})$ <sup>4</sup> was taken as  $1.68 \text{ \AA}^3$  and  $\alpha(\text{Cs}^0)$ <sup>5</sup> as  $67.7 \text{ \AA}^3$ .

To apply (5), it is necessary to evaluate  $R$  and  $\beta$ .  $R$  is the distance from the nucleus of the ion to the metal surface. However, the location of this "surface" is not well defined. Physically it is that plane on which all excess electrons would collect.  $\beta$  is a constant which Sachs and Dexter estimate as  $\beta \cong 0.46$ . However, their approximations appear to make  $\beta$  too high. This is substantiated by Cutler and Gibbons<sup>6</sup> in two instances. For sodium,  $\phi_w(\text{Na-W}) = 0.04$ . Substituting this value in (5) allows us to relate  $R$  and  $\beta$  by minimizing  $\phi$  with respect to  $R$ . Using this relation in (5) gives an expression for  $\phi(\text{Na-W})$  in terms of  $\beta$ .  $\beta$  can now be evaluated by equating  $\phi(\text{Na-W})$  to the reported value of 2.50 ev. The result of this calculation is  $\beta = 0.35$ . From the minimizing relation one obtains  $R = 0.73 \text{ \AA}$ .

Using hard sphere models, the 110 plane of tungsten, and  $R = 0.73 \text{ \AA}$  places the metal surface at  $0.93 \text{ \AA}$  from the plane through the centers of the outermost layer of atoms. This is 70.8 percent of the distance from the center of the surface layer of atoms toward the outermost tangent to the surface, which is a physically reasonable result. There is sufficient

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<sup>4</sup>K. Fajans, and G. Joos, Z. Physik 23, 1 (1924).

<sup>5</sup>R. M. Sternheimer, Phys. Rev. 127, 1220 (1962).

<sup>6</sup>P. H. Cutler, and J. J. Gibbons, Phys. Rev. 111, 394 (1958).

evidence to justify the assumption that for the tungsten emitters the emitting surfaces were essentially 110 planes.<sup>7,8,9</sup>

R was calculated for rubidium and cesium ions on tungsten by the same hard sphere model. In this calculation the same value of  $\beta = 0.35$  was retained, and the same location of the surface as given above was used. The rhenium surface was also assumed to be located 70.8 percent of the distance toward the plane tangent to the outermost layer of atoms. R for cesium ions on rhenium and singly ionized barium<sup>m</sup> on rhenium was also calculated on the basis of a hard sphere model. The emitting face was assumed to be the 0001 plane. For a hexagonal close packed crystal this is the closest packed plane in direct analogy with the tungsten emitter. While Eq. (6) is not exact (the polarization term considers only dipole-dipole interactions) the results obtained (table I) are generally good. Two of the systems considered have calculated values within 20 percent of the experimental values, while the other two ( $\text{Cs}^+\text{-W}$ ;  $\text{Ba}^+\text{-Rh}$ ) are within 10 percent.

For the adsorption of alkali ions, it is seen that the major bonding is due to the image force of the net charge of the ion. However, for barium, the polarization contributes most. Even among the alkali metals, the polarization effect cannot be neglected as it is primarily the difference in polarizabilities that accounts for the heat of adsorption of Cs on W being higher than that of Rb on W.

The author wishes to thank K. P. Luke for suggesting the problem.

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<sup>7</sup>J. A. Becker, Advances in Catalyses, vol. 7 (Academic Press, Inc., (1955).

<sup>8</sup>F. L. Hughes, and H. Levinstein, Phys. Rev. 113, 1029 (1959).

<sup>9</sup>J. B. Taylor, and I. Langmuir, Phys. Rev. 44, 423 (1933).

TABLE I. - PHYSICAL QUANTITIES NECESSARY FOR USING EQ. (5) AND  
COMPARISON OF EXPERIMENTAL AND CALCULATED HEATS OF ADSORPTION

System	$\alpha, \frac{10}{\text{\AA}^3}$	Ionic radii, $\frac{11}{\text{\AA}}$	$R, \frac{\text{\AA}}{\text{\AA}}$	$\phi_i, \text{ev}$	$\phi_w, \text{ev}$	$\phi_{\text{calc}}, \text{ev}$	$\phi_{\text{exp}}, \text{ev}$
Na <sup>+</sup> -W	0.152	0.95	0.73	2.460	0.037	2.50	2.50 <sup>12</sup>
Rb <sup>+</sup> -W	2.920	1.48	1.44	1.875	0.398	2.27	1.90 <sup>7</sup>
Cs <sup>+</sup> -W	5.600	1.69	1.69	1.660	0.632	2.29	2.16 <sup>13</sup>
Cs <sup>+</sup> -Rh	5.600	1.69	1.69	1.660	0.632	2.29	2.01 <sup>14</sup>
Ba <sup>+</sup> -Rh	20.328	1.53	1.48	1.823	2.668	4.49	4.71 <sup>14</sup>

<sup>10</sup>R. M. Sternheimer, Phys. Rev. 127, 1220 (1962).

<sup>11</sup>L. Pauling, The Nature of the Chemical Bond (Cornell University Press, 1960).

<sup>12</sup>R. L. L. Bosworth, Proc. Roy. Soc. (London), A150, 58 (1935).

<sup>13</sup>This value is an average of the values reported in the four following reports:

<sup>a</sup>J. B. Taylor, and I. Langmuir, op. cit.

<sup>b</sup>J. A. Becker, Advances in Catalysis, vol. 7, (Academic Press, 1955).

<sup>c</sup>M. D. Scheer, and J. Fine, Jour. Chem. Phys. 37, 107 (1962).

<sup>d</sup>J. M. de Boer, and C. F. Veenemans, Physica 1, 960 (1933).

<sup>14</sup>M. D. Scheer, and J. Fine, Jour. Chem. Phys. 38, 307 (1963).